Inorganica Chimica Acta, 25 (1977) L53–L54
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Boron–Nitrogen Compounds. LXIX*. Photochemical Synthesis of 10-Phenyl-8,9-diaza-10-boraphenanthrene

K. D. MÜLLER and K. NIEDENZU

Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506, U.S.A.

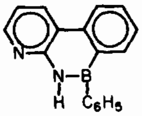
Received September 13, 1977

Very little is known about the photochemical behavior of organoboranes and most photochemical studies of boron compounds deal with mechanistic problems. The only known example of a preparative-scale photochemical synthesis of a boron–nitrogen heterocycle was described for the oxidative photocyclization of (anilino)diphenylboranes; the resulting 9,10-azaboraphenanthrenes are exceedingly stable towards hydrolysis and oxidation [2, 3].

In contrast to (anilino)diphenylboranes, the chemically related (2-pyridylamino)diphenylborane is quite insensitive to atmospheric moisture at room temperature [4, 5]. This unexpected hydrolytic stability is due to internal coordination of the pyridine nitrogen with the boron atom, and a cyclic dimeric structure has been established for (2-pyridylamino)diphenylborane [5]. It was assumed that under photo-impact this dimer would dissociate and the resultant monomer could undergo a cyclization similar to that of (anilino)diphenylboranes. On the other hand, such a photocyclization of a borane substituted by a nitrogen heterocycle has not been studied previously.

Results and Discussion

Surprisingly, the photocyclization of (2-pyridylamino)diphenylborane did not occur when the aminoborane was subjected to photolysis. However, when (2-pyridylamino)diphenylborane was generated by a photoreactor (by mixing a solution of 2-aminopyridine and (diphenyl)chloroborane in cyclohexane) with subsequent irridation of the mixture in the presence of iodine, the desired 10-phenyl-8,9-diaza-10-boraphenanthrene, I, was obtained.



The first step of the reaction, *i.e.* the formation of the (2-pyridylamino)diphenylborane, appears to influence the yield of the photocyclization. Thus, no diazaboraphenanthrene was formed on irridation when the mixture of 2-aminopyridine and (diphenyl)-chloroborane was stirred for only 45 minutes; allowing for reaction times of more than 150 minutes, however, produced the desired photoproduct.

10-Phenyl-8,9-diaza-10-boraphenanthrene is a slightly yellow, crystalline material which is readily soluble in hexane, cyclohexane, CCl_4, or methanol. The UV spectrum of the heterocycle in cyclohexane exhibits two characteristic absorptions at 318.5 nm and 332 nm (ϵ = 2990 l/mol cm and ϵ = 3350 l/mol cm) thus indicating the pseudoaromatic character of the B–N–C heterocycle [6]. (2-Pyridylamino)diphenylborane shows only one high wavelength UV absorption at 298 nm (ϵ = 4570 l/mol cm) in tetrahydrofuran or at 295 nm (ϵ = 3320 l/mol cm) in methanol.

10-Phenyl-8,9-diaza-10-boraphenanthrene is hydrolytically and photochemically remarkably stable. Neither addition of water or methanol nor prolonged irridation of the reaction mixture caused any changes in the UV spectra of the particular samples. The compound also appears to be completely stable when exposed to atmospheric moisture.

The infrared spectrum of I (in CCl_4) exhibits a single, very sharp and strong NH stretching mode at 3400 cm^{-1}. In KBr pellet, however, two very broad NH absorptions are observed at 3390 and 3200 cm^{-1}, respectively, indicating an intermolecular association in the crystalline material, presumably via hydrogen bridge bonding between the NH group and the pyridyl nitrogen. Similarly, a CCl_4 solution of 10-phenyl-9,10-azaboraphenanthrene shows only one, very sharp and strong NH stretching band at 3409 cm^{-1}, whereas a doublet of sharp and equally strong NH absorptions appear at 3374 and 3367 cm^{-1}, respectively, when the spectrum is recorded on a KBr pellet of the material.

The UV spectrum as well as the mass spectrum of I seem to support its formulation as a heteroaromatic fused ring system [7]. The mass spectrum shows a fragment corresponding to the molecular ion M^+ with a relative intensity of 92% (the base peak is $(M - 1)^+$). The second set of peaks of significant intensities corresponds to the doubly charged molecular ion M^{2+} (15%), and even a triply charged species $(M - 1)^{3+}$ can be detected (2%); fragmentations are of very low abundance.

Based primarily on mass spectroscopic evidence, the photolysis of $(C_6H_5)_2B{-}O{-}B(C_6H_5)(NH{-}2{-}C_5H_4N)$, which also has a coordinated cyclic structure [5], leads to the formation of triphenylboroxine and (2-pyridylamino)diphenylborane; some benzene formation is also observed. On the other hand, preliminary results indicate that the oxidative photocycliza-

---

*For part LXVIII see ref. 1.

tion of (1-pyrazinylamino)diphenylborane yields 10-phenyl-5,8,9-triaza-10-boraphenanthrene. Thus, the photochemical reactions of (amino)diphenylboranes containing unsaturated nitrogen heterocycles bonded to boron seem to provide access to a variety of new organoboron-nitrogen heterocycles.

Experimental

Cyclohexane was distilled from a mixture of sodium and benzophenone shortly before use. 2-Aminopyridine (Reilly Tar and Chemical Corporation, Indianapolis, Indiana) was purified by recrystallization from hexane and subsequent vacuum sublimation (bath temperature 40 °C at 1 Torr). (Diphenyl)chloroborane was prepared as previously described [9]. Melting points were determined using a Mel–Temp block.

A NORMAG falling-film photoreactor (Otto Fritz GmbH, Hofheim, Germany) equipped with a high-pressure mercury lamp HANAU TQ 150 was used for the photoreactions. Infrared spectra were recorded using a Perkin–Elmer Model 621 spectrometer employing standard operating conditions, ultraviolet spectra were recorded on a Beckman Model 26 instrument. Mass spectral data were obtained using a Perkin–Elmer–Hitachi RMU-7 mass spectrometer (70 eV; source temperature = 180 °C).

10-Phenyl-8,9-diaza-10-boraphenanthrene

A solution of 2.13 g (22.7 mmol) of 2-aminopyridine in 1300 ml of cyclohexane is prepared in the photoreactor under nitrogen cover and a solution of 2.14 g (10.7 mmol) of (diphenyl)chloroborane in 15 ml cyclohexane is added dropwise over a period of 15 minutes. The mixture is stirred at room temperature for 2.5 h and 20 mmol of iodine are added. The solution is then irradiated using the mercury lamp in a quartz inset. Progress of the reaction can be followed by withdrawing 0.1 ml samples, diluting them with 3 ml of cyclohexane and examining the ultraviolet spectrum; after 7 to 8 h the absorptions at 318.5 and 332 nm usually reach a maximum indicating the end of the reaction. The reaction mixture is removed from the photoreactor, washed with four 300-ml portions of water, four 100-ml portions of 10% HCl, three 80-ml portions of dilute sodium sulfite solution, four 100-ml portions of 1% aqueous NaOH, and finally three 100-ml portions of water. The cyclohexane layer is then dried with sodium sulfate and evaporated to yield 0.4 g of slightly yellow product, melting point (after recrystallization from hexane) 166–168 °C (with decomposition).

IR spectrum (KBr pellet; frequencies in cm^{-1}; abbreviations: vs = very strong, s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, b = broad): 3370, m,b; 3200, s,b; 3150 s,sh; 3100 m; 3075 s; 3050 s; 3020 m,sh; 3000 m,sh; 1590 vs; 1578 m,sh; 1560 s; 1540 m,sh; 1510 m; 1490 m,sh; 1470 m, 1440 vs; 1430 vs; 1418 vs; 1345 m,sh; 1325 s; 1315 s,sh; 1300 vs; 1280 s; 1255 m,sh; 1213 m; 1158 w; 1126 w; 1068 w; 1000 m; 925 w; 907 w; 870 m; 855 w; 810 vw; 778 s; 763 s; 751 s; 740 s; 697 s; 650 w; 636 vw; 620 vw; 590 w; 576 m,sh; 570 m.

Mass spectral fragmentation (relative intensities (in parentheses) greater than 5%): m/e = 257 (17.3), 256 (92.5), 255 (100), 254 (29.3), 253 (5.3), 179 (5.3), 152 (5.9), 128 (10.6), 127.5 (14.9), 127 (11.2).

Acknowledgments

One of the authors (K.-D. M.) thanks the Deutsche Akademische Austauschdienst for a NATO fellowship. The present work was partially supported by the Kentucky Tobacco and Health Research Institute and the authors are grateful to Reilly Tar and Chemicals Corporation, Indianapolis, Indiana, for a generous gift of 2-aminopyridine.

References

1 K. Niedenzu, K.-D. Müller, W. J. Layton and L. Komorowski, *Z. Anorg. Allg. Chem.*, in press (1977).

2 P. J. Grisdale and J. L. R. Williams, *J. Org. Chem., 34,* 1675 (1968).

3 P. J. Grisdale, M. E. Glogowski and J. L. R. Williams, *J. Org. Chem., 36,* 3821 (1971).

4 B. R. Gragg, R. E. Handshoe and K. Niedenzu, *J. Organometal. Chem., 116,* 135 (1976).

5 B. R. Gragg and K. Niedenzu, *J. Organometal. Chem., 117,* 1 (1976).

6 M. J. S. Dewar, V. P. Kuppa and R. Pettit, *J. Chem. Soc.*, 3073 (1958).

7 R. C. Dougherty, *Tetrahedron, 24,* 6755 (1968).

8 K. Niedenzu, H. Beyer and J. W. Dawson, *Inorg. Chem., 1,* 738 (1962).